

**A STUDY ON DEVELOPMENT OF
AN ARSENIC TEST KIT AND
SOME ARSENIC CONTAMINATION ISSUES**



ITN-BANGLADESH
Center for Water Supply & Waste Management
BUET, Dhaka, Bangladesh

242-03ST-18142

**A STUDY ON DEVELOPMENT OF AN ARSENIC TEST KIT AND
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ITN Research Series 05

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Published by

ITN-Bangladesh

Centre for Water Supply and Waste Management
(A project financed by DANIDA)
Civil Engineering Building (3rd Fl.)
BUET, Dhaka-1000
Bangladesh

June, 2003

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Cover Design by: Mr. Khairuzzaman Biplob

Printed by : Matiar Manush, 173 Fakirapool (1st. Fl.), Dhaka-1000; Ph.- 0171 661841

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FOREWORD

Since arsenic was detected in groundwater, detection and measurement of arsenic in the field level became a major problem in the study of arsenic contamination. Several types of field kits were available but all of them produced extremely toxic arsine gas and used toxic mercuric bromide paper for development of colour to compare with standard colour chart. The accuracy of measurement by the field kits was not upto the desired level. At the same time, a need for development of arsenic removal technology using local indigenous materials was felt badly. A low cost technology, attached to the tubewell or suitable for use at household level could save millions in terms of cost of red marked tubewell destined to out of operation.

ITN-Bangladesh took this project of developing an arsenic test kit and investigating into the arsenic removal capacities of indigenous materials available at local level in Bangladesh. The field kit developed under this project used non-toxic Silver Nitrate soaked papers instead of toxic Mercuric Bromide paper as indicator and successfully measured arsenic in the range 20 to 70 $\mu\text{g/L}$ with reasonable accuracy. But problem remains that the black and white shades produced by metallic silver at different concentrations of arsenic become fade very quickly giving error, if delayed in taking reading or test is conducted in direct sunlight. Production of stable colour in all conditions needs further research. Adsorption capacities of arsenic by different materials were tested in the laboratory, in which good removal potentials were found in Bijoypur clay, bleached sawdust and newspaper pulp.

I hope this publication will provide guidance to researchers willing to continue their research in this direction.

M. Feroze Ahmed
Centre Director

SUMMARY

This report is organized in 6 chapters. Chapter 1 provides an overview of the parameters responsible for the adverse of arsenic from mineral forms into groundwater and also of the basic principles that regulates the chemistry and biochemistry of arsenic as a toxic element. Assuming the suggested presence of arsenopyrite in Bangladesh soil, solubilisation of arsenic was viewed as the consequence of air oxidation of this mineral. Geological transformation of water tables, blockage of the periodic recharging of aquifers and changes even of freshwater flow pattern can cause arsenic build up in groundwater. In Bangladesh, reducing environment in the aquifer is probably the main cause of arsenic dissolution in water. The section on chemistry and biochemistry of arsenic addresses issues such as the mechanism of arsenite binding to proteins and the substitution of phosphate by arsenate in genes as the reasons for arsenocosis leading to cancer. The possibility of treating arsenocosis by drugs is also mentioned.

Chapter 2 presents the objectives of this project including its workplan and time schedule. The objectives include designing a field kit for the semi-quantitative detection of arsenic, searching mitigation methods, and determining the seasonal variation, arsenic speciation, and speciation of co-occurring ions in groundwater. The locations of the nine tubewells and the way the water samples were collected and preserved are mentioned. The methods for chemical analysis and the grades of chemicals used are discussed.

Chapter 3 presents a description of the kit box designed for the semi-quantitative detection of arsenic in the field. The chemistry behind the detection method and the arsenate–arsenite interconversion reactions are included. The kit has an H_2S -guard. The detection method is based on AsH_3 generation, which leads to the development of a dark spot of silver deposit in a test paper. The darkness is compared with that on a standard colour strip to assess the concentration of arsenic in the sample. The detection procedure, described in 8 steps, is followed by description of the chemicals and equipment used and the manner in which they are prepared and stored. The advantages and disadvantages of the method, including suggestions for further improvement, are discussed. The kit can semi-quantitatively detect arsenic at 20-70 ppb . With a few exceptions, the materials used in the kit are all local and the cost per sample analysis is 20 Taka.

Chapters 4-6 are based on experiments. Chapter 4 deals with arsenic removal from synthetic samples prepared in the laboratories and actual groundwater

samples collected from tubewell. Adsorption was carried out in basic, neutral and acidic medium on solid surfaces such as activated charcoal, powdered brick, Bijoypur clay, sawdust, newspaper pulp, jute fibre, cellulose-Fe(OH)₃ composite and synthetic polymers. With a few exceptions everything adsorbed arsenic. Most materials adsorbed arsenic well in acidic medium, while no adsorption took place in basic medium. The cellulose-Fe(OH)₃ composite sorbed arsenic the most. The mechanism of adsorption is discussed. Arsenic removal using precipitation was studied. Alums were found to precipitate arsenic. Simple aeration produced light brown precipitate and removed arsenic from groundwater. This finding can be used to develop small-scale domestic arsenic removal units. Treatment of arsenic sludge requires much the same attention as the mitigation technology.

Chapter 5 presents the speciation of arsenic in nine selected tubewells once every month for nine months during Jun 1998 – Feb 1999. Measurements were done by Stripping Voltammetry. Total-arsenic and As^{III} were measured in 79 and 24 samples respectively. The values were analyzed statistically and represented graphically. Some trends were noticed. The arsenic concentration in a tubewell was found to be constantly changing. In many samples, the arsenite concentration was found to be significantly high. In the depth ranges of 40-50 feet and 70-90 feet the tubewells were found low and high in arsenic respectively. Total- arsenic was relatively high during rainy season.

Chapter 6 presents the speciation of co-occurring ions in one groundwater sample. The sample showed high arsenic but very low in sodium, potassium and calcium ions. The amount of arsenic adsorbed and the pH of the soil-water system were assumed to be interrelated. An inverse relationship between the concentration of arsenic in groundwater and those of sodium, potassium and calcium is implicated.

1. INTRODUCTION

1.1 GENERAL

The atomic number of arsenic is 33. With a crustal concentration of 1.5 ppm it is the 48th element in order of abundance¹. Arsenic is a poison in all its forms. Drinking water from tubewells, about 10 million, across Bangladesh, was once taken in good faith to be safe. Now this water has led to a case of mass poisoning in view of the eventual widespread contamination of the country's groundwater with arsenic.

By one estimation², about 35 per cent of the tubewells are unsafe, that is, they have arsenic concentration in excess of the current maximum contaminant level, MCL, of 50 ppb. The WHO provisional Guideline value for arsenic in drinking water is 10 ppb. It should be mentioned that several countries are working to reduce the MCL below 50 ppb.

Indeed, any arsenic related action programme in Bangladesh should have in the list of priorities issues such as categorising tubewells into safe or unsafe, devising mitigation methods, identifying arsenic species in groundwater, revealing the reasons for their formation, and exploring the geochemical factors for the recent adverse shift of arsenic from rocks and soils into waters.

For obvious reasons the present work necessitates experiments on detection and mitigation of arsenic in groundwater as well as experiments related to the seasonal variation of arsenic and the co-occurring ions in groundwater.

1.2 HYDROMETALLURGY OF ARSENIC

Hydrogeological studies related to the origin and extent of arsenic release in Bangladesh and adjoining West Bengal groundwater may lead to a new order in science and technology with respect to environmental protection and preventive rules to be followed in any long-term action programme.

The problem, therefore, requires global attention for arsenic related studies, particularly those involving epidemiological, risk assessment, and dose response investigations.

Arsenic is ubiquitous, and there exists an equilibrium distribution of arsenic in the two matrices of soil and water. The equilibrium may shift in either direction if natural or man made conditions force it to do so.

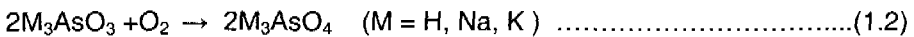
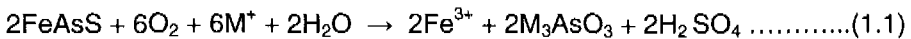
The source of arsenic in Bangladesh was attributed to oxidation of pyritic sedimentary rock such as FeAsS called arsenopyrite. It contains Fe^{II}, As^I and S^I ions in its lattice. But recent studies suggest that arsenic release from soil under reduced conditions in the aquifer is the most likely cause of arsenic contamination of groundwater.

1.3 THE OXIDATION HYPOTHESIS

Early on, the arsenic problem was referred to as the lethal-legacy³ of over irrigation practiced for multiple rice harvests.

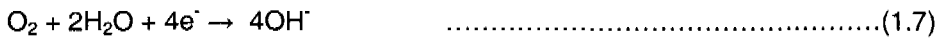
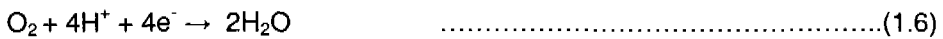
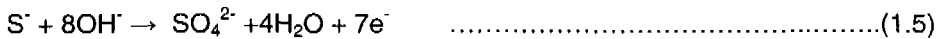
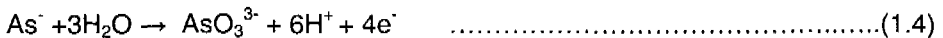
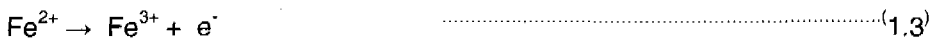
Chemical oxidation of minerals by air, entering underground through bore holes on tubewell sites and or as a result of a dropping groundwater level, produces soluble compounds of arsenic.

In an ideal circumstance, the Fe^{II}, arsenide and sulfide ions on the surface of FeAsS would initially form Fe^{III}, sulfate, and arsenite ions as a result of anodic oxidation in a localised galvanic cell⁴ resembling metal corrosion. At the rock-oxygen-water interface arsenite would get converted to arsenate in the cathodic reduction process. The over simplified redox process is represented by Reaction 1.1:



The resulting arsenate may appear in groundwater as soluble complexes such as Fe(H₂AsO₄)²⁻ and Fe(HAsO₄)⁺ if the acidity is high.

Reaction 1.1 releases sulfuric acid and solubilises arsenic. The acidity helps maintain a reducing atmosphere in presence of ions such as Fe^{II}. Reaction 1.1 depends on the pE-pH^a of the soil-water system and may occur as a result of the following or many other possible half – reactions:



a: pE = -log of E° and pH = -log of [H⁺]

These reactions compete with each other and eventually a localized reaction brings equilibrium or steady state condition that ensures the presence of one set and the removal of another set of chemical substances from the groundwater in a locality.

At low acidity if Fe^{3+} and AsO_4^{3-} are the end products, groundwater samples will contain no arsenic for FeAsO_4 has a very low solubility as indicated by the solubility product^b values shown in Table 1.

Table 1 : Solubility Product^b, K_s , of Some Salts

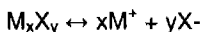
| Salt: Solubility Product | Salt : Solubility Product | Salt : Solubility Product |
|---|---|---|
| $\text{AlAsO}_4 = 1.6 \times 10^{-16}$ | $\text{Ca}_3(\text{AsO}_4)_2 = 6.8 \times 10^{-19}$ | $\text{Fe}(\text{OH})_3 = 4 \times 10^{-38}$ |
| $\text{Al}(\text{OH})_3 = 1.3 \times 10^{-33}$ | $\text{Ca CO}_3 = 2.8 \times 10^{-9}$ | $\text{Fe PO}_4 = 1.3 \times 10^{-22}$ |
| $\text{AlPO}_4 = 6.3 \times 10^{-19}$ | $\text{Ca}_3(\text{PO}_4)_2 = 2.0 \times 10^{-29}$ | $\text{Mg}_3(\text{AsO}_4)_2 = 2.1 \times 10^{-20}$ |
| $\text{Ba}_3(\text{AsO}_4)_2 = 8.0 \times 10^{-51}$ | $\text{CaSiO}_3 = 2.5 \times 10^{-8}$ | $\text{Mg}_3(\text{PO})_2 = 10^{-23}$ to 10^{-27} |
| $\text{CO}_3(\text{AsO}_4)_2 = 7.6 \times 10^{-29}$ | $\text{Pb}_3(\text{AsO}_4)_2 = 4.0 \times 10^{-56}$ | $\text{Zn}_3(\text{AsO}_4)_2 = 1.3 \times 10^{-28}$ |
| $\text{Ni}_3(\text{AsO}_4)_2 = 3.1 \times 10^{-26}$ | $\text{FeAsO}_4 = 5.7 \times 10^{-21}$ | $\text{Mn}_3(\text{AsO}_4)_2 = 2.9 \times 10^{-29}$ |
| $\text{BaSO}_4 = 1.1 \times 10^{-10}$ | | |

If the samples are deficient in heavy metal ions or if the metal ions are present in inaccessible forms, only then AsO_4^{3-} or AsO_3^{3-} will remain in solution with some counter ions such as Na^+ or K^+ and some alkaline earth metals. It may be mentioned that these are over simplified natural processes far from their elaborate descriptions.

If the samples are deficient in heavy metal ions or if such ions are not accessible, AsO_4^{3-} will remain in solution with some counter ions of alkali metals or alkaline earth metals such as Ca^{2+} and Mg^{2+} .

It may be mentioned that these ideas are over simplified compared to the actual elaborate processes.

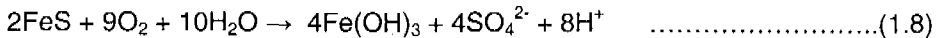
b: Solubility Product : for a sparingly soluble salt M_xX_y , the solubility product is the product of the concentration of ions in a saturated solution. The lower the solubility product, the lower the solubility of a salt. For M_xX_y , the dissociation is :



$$\text{Solubility product, } K_s = [\text{M}^+]^x [\text{X}^-]^y$$

1.4 THE ROLE OF BACTERIA

Bacteria play a role in the hydrometallurgy of many elements. In one mechanism they excrete coenzymes that break down minerals into soluble components which can penetrate the bacterial cell walls within which the digestion process occurs. Microorganisms dependent only on inorganic materials decompose FeS as per Reaction 1.8⁵:



Rock eating bacteria such as, *thiobacillus ferrooxidans*⁴ can carry out bacterial oxidation to produce similar results in both stoichiometric and catalytic reactions.

Arsenite produced initially is further oxidized to arsenate.

As the arsenopyrite dissolves, gold grains, often trapped in the mineral lattice, are liberated. It is thus held that arsenic in groundwater is a predictor of gold in the near by soils and an arsenic track is often used as a pathfinder to gold.

1.5 CHELATION BY HUMIC ACIDS

Humic acids and a variety of other legends in soils and natural waters can release elements from rocks and minerals through chelate formation.

The most important chelating agents that occur naturally are humin, humic acid and fulvic acid. These are degradation-resistant materials formed during the decomposition of vegetation.

Iron and aluminium bind strongly to the humic materials. Other important chelates in nature include pyrophosphate, nitrilotriacetate, carboxylate and heterocyclic nitrogen. For a mineral like FeAsS, if a chelate removes iron, arsenic and sulfur would simultaneously go into solution.

1.6 NATURAL RECHARGING OF AQUIFERS

Recharging of the aquifers by natural waters⁶ carrying ferric hydroxide and oxygen ensures precipitation of their arsenate content and thus removes arsenic systematically from groundwater.

Lack of recharging due to blockade by dams and embankments allows groundwater a longer resident time, which helps, arsenic build up in an aquifer.

Even changing the flow pattern of canals and streams may result in a similar unfavorable distribution. This hypothesis can be checked by C-14 or H-3 labeling techniques.

Groundwater from a water table in a saturated zone is less vulnerable to arsenic contamination than that from an unsaturated or parched water table. Due to geological transformations the character of a water table may change along with the quality of water held in it.

1.7 CHEMICAL AND BIOCHEMICAL FUNDAMENTALS

Arsenic is a member of Group 5A of the Periodic Table and a congener of nitrogen and phosphorus. The electronic configuration of arsenic in the valence level is $4s^2 4p^3$; the stable oxidation states being III and V corresponding to the loss of p and s electrons in succession.

Much of the chemistry of the element involves the interconversion of these two oxidation states. The reduction of As^V to As^{III} takes place in acidic solutions at $E^\circ = 0.56$ volts, whereas the reverse takes place in basic solutions at $E^\circ = -0.67$ volts.

Arsenic – Phosphorus Similarity

It may be mentioned that P^V cannot be as easily reduced as As^V . Another major difference between these two elements is the stability of phosphoric acid esters to hydrolysis, making room for the stable existence of DNA and ATP. Esters of As^V acids are easily hydrolyzed; the half-life in neutral solution being about 30min.

Enzymes can accept arsenate to incorporate into other compounds, but the species so formed hydrolyze immediately. Moreover, AsO_4^{3-} can replace PO_4^{3-} in DNA or ATP. This phenomenon is believed to account for the toxicity of AsO_4^{3-} . Such change in genes could lead to be altered gene expression, which may end up causing carcinogenesis.

The Strong Affinity of Arsenic for Sulfur

The affinity of arsenic for sulfur is revealed in the common occurrence of sulfur containing minerals such as, realgar, As_4S_4 , orpiment, As_4S_6 and arsenopyrite, $FeAsS$. As^{III} is considered to be a stronger poison than As^V . The toxicity of As^{III} compounds is partly affected by its interaction with protein thiols, SH, as shown in Figure 1. Such binding might inhibit the functions of an enzyme.



Figure 1 : A scheme for As^{III} and protein thiol interaction

Removal of Bound Arsenic from Humans

The action of dimercaptol, known as British Anti-Lewisite, BAL, in removing arsenic species from humans is believed to occur through the displacement of a bound arsenic from a protein because of the formation of a more stable complex as shown in Figure 2.

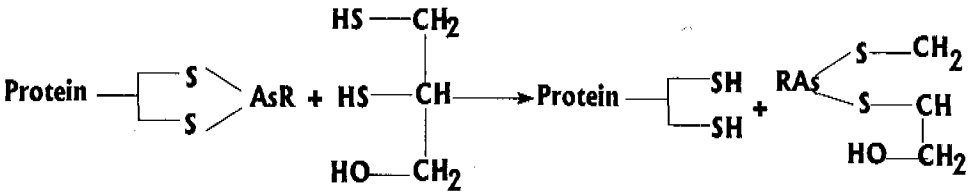


Figure 2: Possible arsenic removal mechanism from humans

Arsenic Species in Waters and Human Foods

Some commonly occurring arsenic compounds in waters and human foods are shown in Table 2.

Table 2 : Arsenic species found Commonly in Waters and Human Foods

| Species | Chemical Formula | Abbreviation |
|-------------------------|--|---------------------------------|
| Arsenious acid | H ₃ AsO ₃ | As ^{III} |
| Arsenic acid | H ₃ AsO ₄ | As ^V |
| Oxythioarsenic acid | H ₃ AsO ₃ S | |
| Monomethylarsonic acid | CH ₃ AsO(OH) ₂ | MMA |
| Methylarsonous acid | CH ₃ As(OH) ₂ | MAA ^{III} |
| Dimethylarsinic acid | (CH ₃) ₂ AsO(OH) | DMA |
| Dimethylarsinous acid | (CH ₃) ₂ As(OH) | DMA ^{III} |
| Trimethylarsine | (CH ₃) ₃ As | TMA |
| Trimethylarsine oxide | (CH ₃) ₃ AsO | TMAO |
| Tetramethylarsonium ion | (CH ₃) ₄ As ⁺ | Me ₄ As ⁺ |
| Arsenocholine | (CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH | AsC |
| Arsenobetaine | (CH ₃) ₃ AsCH ₂ COO ⁻ | AsB |

In addition there are arsenosugars, arsenolipids found in plants and animals and ethylmethylarsines, $\text{Et}_x\text{AsMe}_{3-x}$, ($x = 1-3$) found in natural gas. Arsenosugars and arsenolipids have a pentose unit in each of their structures.

Arsenic Containing Food Additives

Some commercial arylarsenicals approved as food additives are shown in figure 3. Some of these are used in livestock feeds as growth promoter, others are used as preventives against animal diseases.

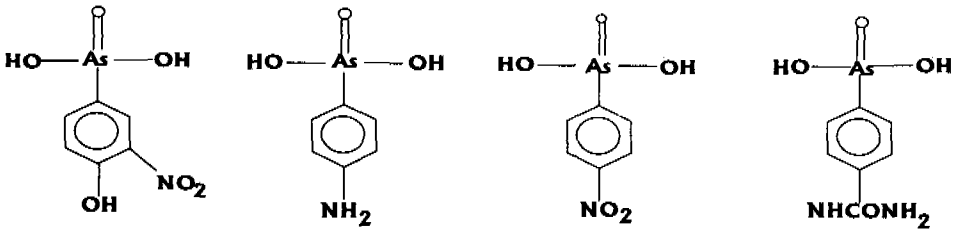


Figure 3 : Structures of some commercial food additives

Biochemical Actions of Arsenic

Arsenic has been used throughout civilization starting as a poison in Greece and Rome. The discovery that syphilis could be successfully treated by arsenic stimulated worldwide interest in the chemistry and biochemistry of arsenic.

Biochemically, arsenic acts to coagulate proteins, forms complexes with coenzymes, and inhibits the production of adenosine triphosphate, ATP, in essential metabolic processes.

Normally a daily intake of 10-50 microgram results in no threat to human health. An established fact is that in humans inorganic arsenicals are skin and lung carcinogens.

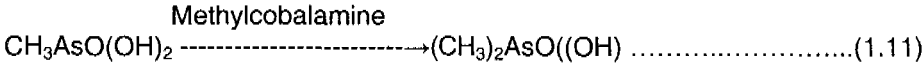
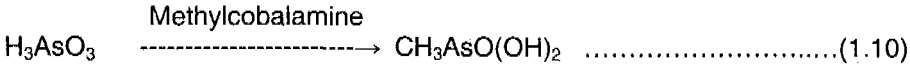
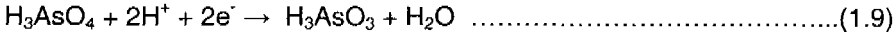
Acute arsenic poisoning can result from the ingestion of about 100 mg of the element. Chronic poisoning occurs with the ingestion of small amounts over a long period of time.

Inorganic and Organic Arsenicals

Inorganic arsenicals are ionic and held strongly by counter ions. They can stay in the body system for longer period than usual.

Organic arsenic compounds on the other hand are covalent and mobile. Biomethylation of inorganic arsenicals produces metabolites that have low reactivity toward most tissues and are readily excreted through urine almost unchanged.

Inorganic compounds are converted to methyl derivatives according to the following reactions:



Arsenic in Water and Groundwater

Drinking water usually contains arsenic as arsenate and, under anerobic conditions, some arsenite.

Methylated species are rare in water supplies unless there exists high biological activity.

Notionally, arsenate is the major species in groundwater, although it is increasingly being shown that arsenite might be more prevalent than expected. Improved sampling methodology, sample preservation, and analytical methods are contributing to the changing observation.

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2. THE STUDY PROGRAM

2.1 THE OBJECTIVES AND WORKPLAN

The work envisages the designing a field kit for the semi-quantitative detection of arsenic close to the MCL and the development of easy mitigation methods so desperately needed to relieve the people living in fear of arsenic.

Both these objectives require knowledge on type and the extent of ions co-occurring in groundwater and the pattern of seasonal variation of arsenic concentration. The strategy was, therefore, fixed in line with the objectives. The work plan and time schedule of the project is shown in Table 3.

- Designing a Field kit for the Semi-quantitative detection of Arsenic.
- Searching Mitigation Methods: Physico – Chemical and Chemical^c
- Seasonal Variation and Arsenic Speciation.
- Speciation of Co-occurring Ions in Groundwater.

Table 3: Workplan and Time Schedule

| WORK | May 98 | June | July | Aug | Sept | Oct | Nov | Dec | Jan 99 | Feb |
|---|--------|------|------|-----|------|-----|-----|-----|--------|-----|
| Speciation of some ions in groundwater: A | A | A | | | | | | | | |
| Mitigation: Phys-chem: B | | | B | B | B | | | | | |
| Mitigation: Chem: C | | | | | | C | C | C | | |
| Temporal Variation:D | D | D | D | D | D | D | D | D | D | D |
| Det. Kit :E | | | | | | | | | E | E |

c: Physico-chemical methods of arsenic mitigation involves processes such as adsorption, chemisorption and ultrafiltration or reverse osmosis. Some of the chemical mitigation methods are flocculation, coprecipitation and trapping through floc formation.

2.2 SELECTION OF TUBEWELLS

Chatkhil thana under Noakhali district being one of the badly affected areas, was chosen as the site for collection of groundwater. Nine locations within a radius of 1.5 km in the thana proper were selected.

Location No 9, because of its high arsenic contamination and the consequent hyperpigmentation of two of the users, was sealed off long ago by the DPHE.

2.3 GENERAL EXPERIMENTAL WORKS

Sample collection and Storage

The groundwater from a tubewell, Location Nos. 1-9, was collected after 25 strokes of the water pump. A sample was stored in a fresh white plastic bottle, up to the brim, after adding 1 mL of HCl per 100 mL of groundwater.

The use of excess Fe^{II} and acidic pH at less than 2 suppress oxidation of arsenite¹, as indicated by Reaction 1.6. Indeed presence of excess Fe^{II} is assumed in these samples.

Materials and Methods

Imported chemicals were collected from the local market and their quality, in some cases, was verified using standard laboratory methods. A.R. AgNO_3 concentrated HCl, NH_4SCN , EDTA, sodium molybdate, lead acetate and arsenic-free zinc were used. Solutions were prepared in deionised or distilled water.

Sodium and potassium were determined by atomic absorption spectrophotometry.

Calcium and potassium were determined together by EDTA titration².

Chloride was determined by Volhard's method.

Phosphate was analyzed by spectrophotometry.

The Gutzeit test was performed frequently to monitor arsenic and stripping voltammetry was used to quantitatively determine As(III) and total arsenic.

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3. DEVELOPMENT OF A FIELD TEST KIT FOR ARSENIC

3.1 INTRODUCTION

Scheele, in 1775, discovered that under reducing conditions arsenic compounds can be reduced to arsine, AsH_3 , a volatile gas¹.

This discovery led to the development of the Marsh test² for the detection of arsenic. Arsine gas is volatilized from the reaction mixture and is detected by decomposition to an arsenic mirror.

The Gutzeit test² is a modification of the Marsh method. In this modification the arsine gas is brought in contact with filter paper soaked with silver nitrate or mercuric bromide solution to produce a coloured metallic deposit.

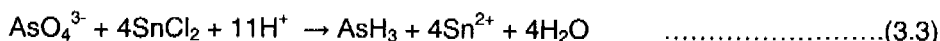
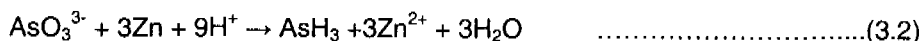
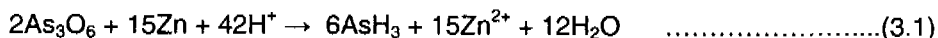
Using either reagent the process can be made semi-quantitative.

The analytical method known as 'hydride generation' is an application of the Marsh-Gutzeit discovery in which reducing agent is sodium borohydride³.

3.2 HYDRIDE GENERATION

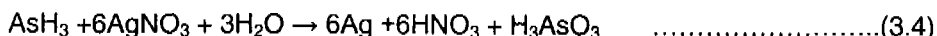
The Zn-HCl system completely reduces As^{III} compounds to AsH_3 , but for As^{V} compounds the reduction is incomplete.

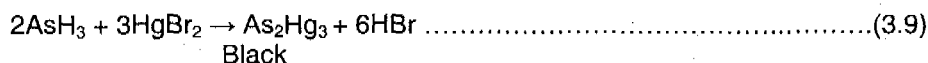
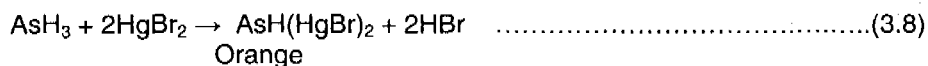
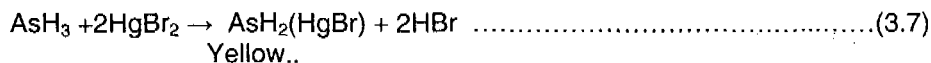
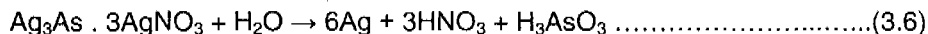
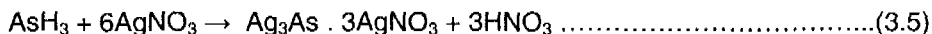
Complete reduction for As^{V} species is achieved by a SnCl_2 -HCl mixture in the presence of I^- ion.



3.3 GUTZEIT TEST REACTIONS

The reactions taking place on the filter paper soaked with AgNO_3 or $\text{Hg}(\text{Br})_2$ solution can be represented as follows:

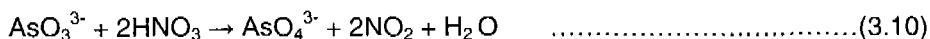




3.4 ARSENATE - ARSENITE INTERCONVERSION

A number of methods are available for the arsenate-arsenite interconversion. In any application the method to be used depends on the type of solvent and the nature of reactants present in the reaction mixture.

Oxidation by nitric acid:



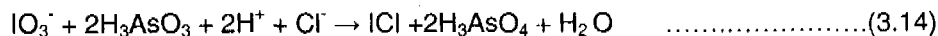
Reduction by Potassium iodide in acidic medium:



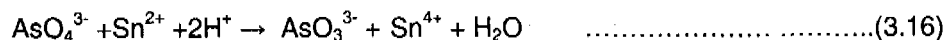
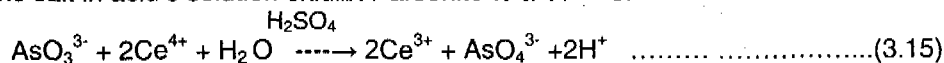
Sodium bisulfite reduction:



Bromate and iodate oxidize arsenite to arsenate:



Ceric salt in acidic solution oxidizes arsenite to arsenate:



3.5 EXPERIMENTAL WORKS

Detection Procedure

- Step 1. Take a water sample up to the mark, 5 mL, in an 18 mL test tube. Use a medicine dropper, if required.
- Step 2. To this volume add 10 drops of Reductor 1 and 3 drops of Reductor 2 and leave the mixture for 15 minutes.
- Step 3. When step 2 is in progress, put a filter paper segment on the mouth of the H₂S guard. This is a small tube attached to a rubber bung at the narrow end and containing a puff of cotton impregnated with lead nitrate. Hold the segment in place with the help of a rubber band. Place a drop of the Sensor on the filter paper.
- Step 4. At the end of the 15-minute period put 5 granules of zinc into the liquid. Quickly fix the rubber bung of the H₂S – guard on the test tube.
- Step 5. Hold the test tube with the help of a test tube holder. Heat the liquid for 3 minutes on a low flame of a spirit lamp.
- Step 6. At the end of the heating time remove the filter paper. A dark spot indicates the presence of arsenic in the sample.
- Step 7. Judge the concentration of arsenic in the sample by matching the spot resulted with those on the standard arsenic concentration strip. A deeper colour indicates a higher concentration of arsenic.
- Step 8. Wash the test tube and zinc granules 3 times with surface water and finally rinse once with distilled water. Drain the washings every time carefully and do the next test.

Chemicals and Equipment Used

Chemicals are either lab or analytical grade.

Reductor 1: A 5 per cent solution of SnCl₂ · 2H₂O in concentrated AR HCl, the solution being cleared by heating it with added metallic tin. The HCl has 0.000005 per cent arsenic.

Reductor 2: A 100 per cent solution of KI in water.

Metallic Zinc : Zinc granules containing 0.000015 per cent arsenic.

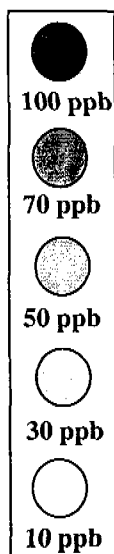
Sensor : A 12 per cent solution of AgNO_3 in water .

H₂S Guard: 0.015 g of cotton wool soaked with one drop of 33 per cent $\text{Pb}(\text{NO}_3)_2$ and dried.

Synthetic Samples: These were obtained by dissolving in water lab grade $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ of BDH.

Test Tube : Length 12.5 cm and inner diameter 1.5 cm.

Filter Paper: Ordinary filter paper cut into four equal segments.



Colour Chart

Figure 4 : Chemicals and accessories with colour chart for the arsenic field kit

3.6 OUTCOME

The Kit Box

A well built kit box made of low cost wood of dimension 25.3cm x 16.2cm x 19.8cm and volume about 8 L was shaped by designer.

Based on the Gutzeit method the kit contains items as indicated in Table 4. It has a sulfide correction unit called the H₂S-guard.

Table 4: Arsenic Detection kit for 150 Samples

| SI.No | Item | Number: Quantity | Cost, Taka |
|-------|---|--------------------|-------------|
| 01 | Wooden Box | 1 | 150 |
| 02 | Test-tube and test tube holder | 2+1 | 10+19 |
| 03 | Filter paper: ordinary | 100 segments | 75 |
| 04 | Zinc granules | 20g or 50 granules | 200 |
| 05 | Reductor 1 | 50 mL | 600 |
| 06 | Reductor 2 | 30mL | 700 |
| 07 | Sensor | 20mL | 450 |
| 08 | H ₂ S guard | | 100 |
| 09 | Rectified spirit | 4x200mL | 140 |
| 10 | Distilled water | 50x100mL | 100 |
| 11 | Spirit lamp | 1 | 35 |
| 12 | Box of matches | 1 | 1 |
| 13 | Dropper with rubber teat | 2 | 20 |
| 14 | Reagent bottles: 3x50mL and 1x200 ml with stopper | 3+1 | 200 |
| 15 | Earthen pot | 1 | 10 |
| 16 | Plastic wash bottle, 100mL | 1 | 20 |
| | Total cost | | 2830 |
| | Cost: per sample detection | | 20 |

Standard Arsenic Concentration Strip

At the end of an experimental run the segment of the spotted filter paper was dried in an oven at 110°C for 10 minutes.

Upon cooling the coloured spot was covered with a thin coating of wax by rubbing mildly with the bottom edge of a candle.

The segment was then washed by alternate dipping into and withdrawing from the distilled water 100 times and finally dried at 110° C for 10 minutes.

A circular spot was then cut off from the coloured deposit and put on the strip which was covered with polythene.

A 10-70 ppb concentration range used as well as one at 100ppb. Synthetic arsenic samples at 10 ppb intervals were used to develop the spots. The strip begins with a blank filter paper marked as 00 ppb.

3.7 DISCUSSION

This kit can semi-quantitatively detect arsenic in the range of 20-70 ppb by comparing the colour spot obtained in a test with that on the standard colour strip. Below 20 ppb the colour is light and inconclusive, above 100ppb the colour is dense and again inconclusive.

The colour of the spot on the filter paper is dark. The colour is due to finely divided metallic silver. The kit uses mostly local materials and the cost per sample is about 18-20 Taka .

The kit uses silver nitrate and avoids mercury as the latter itself is a poison. Moreover silver nitrate is locally available.

Under field conditions, silver nitrate decomposes to give dark, messy product. This can be avoided by wrapping the bottle containing the solution of silver nitrate with carbon paper.

The intensity of the colour on the filter paper depends on the diameter of the H₂S-guard. This makes the test result specific to the H₂S-guard .

To avoid an H₂S-guard, the puff of cotton wool soaked with lead nitrate solution can be put just below the neck of the 18 mL test tube. The filter paper segment can be held on the mouth of the test tube with the help of a rubber band.

Because of air oxidation Reductor 2 develops a red colour with time. This can be stopped by adding few drops of Reducror 1 to Reductor 2.

The dark colour on the standard colour strip fades with time. This may be due to an interaction between metallic silver and items like polythene, cellulose, sunlight, wax, air molecules and arsenic acid. Cellulose is a reducing agent, and a negative oxidation state is not known for silver.

So, oxidation of silver is the only alternative. An antioxidant such as ascorbic acid added to the spot on the standard colour strip may prevent fading.

3.8 RECOMMENDATIONS

Comprehensive studies are needed to find a low-cost and easy method for the routine semi-quantitative and quantitative measurement of arsenic not only in water but also in urine. The best route for the body to excrete arsenic is through the urine.

Arsenic is ubiquitous. Therefore, utmost care is needed for the reproducibility and legitimacy of a result .In effect, every kit must have its own colour strip.

Further studies are necessary to make the colour on the strip permanent.

Alternatively, the colour spots on the filter paper segment can be replicated using computer simulation and a colour printer.

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4. ARSENIC REMOVAL METHODS

4.1 INTRODUCTION

The seven best available technologies¹ in arsenic removal performance are coagulation- filtration, lime softening, activated alumina treatment, anion exchange, reverse osmosis, electro dialysis reversal and nanofiltration.

These are all large-scale methods but can be modified to match the situation in Bangladesh.

Alternatively small to mid size utility methods can be developed aiming at supplying safe water to every household. The present work aims at exploring methods to remove arsenic from tubewell water using cheap and readily available materials.

Very simple mitigation methods can be aeration of contaminated tubewell water or its alum treatment.

Aeration oxidizes arsenic and the co-occurring iron which then precipitate as FeAsO_4 .

Alums and other chemicals added as coagulants alter the physical state of dissolved and suspended particles and facilitate their removal by sedimentation. In the dispersed phase these particles remain electrically charged, usually negative. As a result of alum addition the surface charge of suspended particles is lessened or the thickness of the diffuse electric layer is reduced by cations, such as Al^{3+} , Fe^{3+} or Cr^{3+} , which have high charge-size ratio.

They form large hydrolyzed metal ions² which bring about particle aggregation either through entrapment within their own voluminous precipitate, through adsorption or bridging

The factors affecting arsenic removal by coagulation are the Oxidation State of arsenic and its initial concentration, coagulant dosage, pH and the presence of co-occurring inorganic solutes.

4.2 EXPERIMENTAL WORKS

A R grade chemicals were used. The Gutzeit test was performed frequently to monitor arsenic and stripping voltammetry was used to quantitatively determine As^{III} and total arsenic.

Bijoypur clay collected from a stock of People's Ceramic Industry and Pulverized ceramic brick were used.

Jute fibre was delignified by digestion in commercial sodium hypochlorite solution having 5-9 per cent chlorine.

Sawdust was bleached using $\text{Ca}(\text{OCl})\text{Cl}$ powder.

The cellulosic materials were finally treated with 6M HCl to remove any adsorbed metal ions from the surface. They were then washed until the washings were neutral to litmus.

The adsorption properties of cellulosic materials were investigated in static or batch and dynamic or column experiments. The static ones were performed with or without shaking.

Field experiments of the static type, using newspaper pulp, were performed at Chatkhil, Noakhali, using water from Location No.8.

An adsorbent was dispersed in 5 mL synthetic or contaminated water sample to which an equal volume of vinegar with 20 percent acetic acid or 6M HCl was added in a 100 mL Erlenmeyer flask.

Preparation of cellulose- $\text{Fe}(\text{OH})_3$ Composite

Newspaper pieces in water pulped in a blender. A precipitate of $\text{Fe}(\text{OH})_3$ was prepared in a 250 mL beaker by adding dilute ammonia drop wise to an aqueous solution of ammonium ferric alum.

The pulp was then mixed with the precipitate and the mixture was stirred thoroughly for ten minutes. The hydroxide quickly became fixed to the cellulose fibre. This is the cellulose- $\text{Fe}(\text{OH})_3$ composite; it was washed on a Buchner funnel to remove excess reagents.

In a glass tube, alternate beds of this material and sand, with a total bed volume of about 48 mL were prepared to pass the contaminated water through.

The coated material, which was found to resist bacterial putrefaction, is a good adsorbent for As^{III} and As^V species. A model arsenic removal unit using iron oxide coated sand has been designed previously³.

4.3 RESULTS

Mitigation Methods: Physico-Chemical

The results of adsorption experiments are summarized in Table-5.

Table 5: Adsorption of Arsenic on Solid Surfaces at 29-30°C

| Adsorbent | Mass of Adsorbent, g | [As], in ppm | Vol of water sample, mL | Neutral medium | Medium acidified with vinegar or HCl |
|----------------------|----------------------|--------------|-------------------------|------------------------|--|
| Activated charcoal | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Calcium tartrate | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Pulverized brick | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Bijoypur clay | 0.4 | 0.5 | 10 | Adsorption takes place | Complete removal after 12h without shaking |
| Smashed sajna seed | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Fresh tamarind | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Untreated sawdust | 0.5 | 0.5 | 10 | No adsorption. | No adsorption. |
| Bleached sawdust | 0.5 | 0.5 | 10 | No adsorption. | Complete removal after 7h without shaking |
| Newspaper pulp | 0.5 | 0.5 | 10 | No adsorption. | Complete removal after 6h without shaking |
| Untreated jute fibre | 0.5 | 0.5 | 10 | No adsorption. | No adsorption |
| Bleached jute fibre | 0.5 | 0.5 | 10 | No adsorption. | Adsorption |

Adsorption of Cellulosic Materials

Cellulosic materials such as sawdust, jute fibre and newspaper pulp were found to adsorb both As^{III} and As^V in acidified synthetic and source waters.

Properties of the adsorbents were investigated in static and dynamic experiments. The static ones were carried out with and without shaking.

Adsorption on Clay Minerals

The clay minerals have active groups such as Si--O--Si, Al--O--Al or Al--O--Si. Presumably an oxygen atom on the surface takes up a proton and the resultant positive centre attracts the protonated oxo anions of arsenic.

The electrostatic attraction combines with the surface force to bring about the perceived adsorption in neutral and acidic solutions. Arsenic adsorptions by soil and clay minerals have been studied⁴.

Adsorption on Synthetic Polymers

Polystyrene and foam were also found to adsorb arsenic. Polystyrene charged with cellulose-Fe(OH)₃ composite may potentially be used in arsenic filters for domestic use.

Mitigation Methods: Chemical Arsenic Removal by Flocculation

Removal of arsenic from groundwater was tried by flocculation with Al³⁺ and Fe³⁺ ions having high charge to size ratio. When (NH₄)Fe(SO₄)₂ · 12H₂O is dissolved in water, the Fe³⁺ hydrolyses. Eventually Fe(OH)₃ is formed which coprecipitates with arsenic.

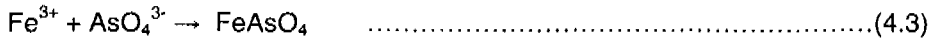
Also, potash alum, KAl(SO₄)₂ · 12H₂O, locally known a 'Fitkari' produces a similar affect obviously through the formation of Al(OH)₃.

The risk of using these reagents is the introduction of additional ions to the water to be purified. Also, it is seen that, after the alum treatment, water loses its palatability and, as such, the method is not readily acceptable.

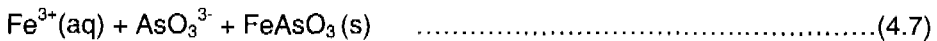
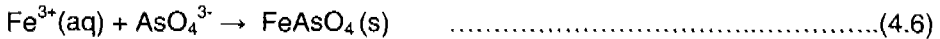
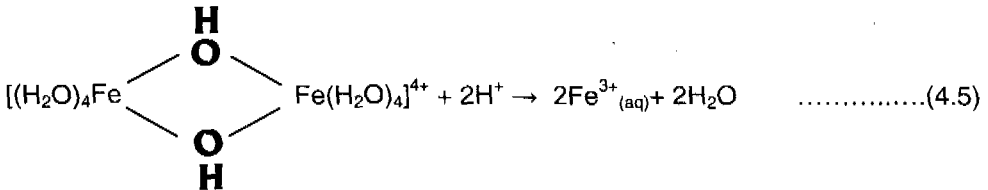
Arsenic Removal by Simple Aeration

An amount of groundwater from Location No. 8 was stored in an open glass container. After 5 days a light brown, gelatinous precipitate was found at the bottom of the container and the clear water on top showed no arsenic. The precipitate could be FeAsO₄ and the reason for its formation might be the result of the following reactions:





Alternatively the neutralization of the colloidal hydroxide, caused by the acidity developed on account of carbon dioxide dissolution, could eventually lead to the formation of precipitate of arsenate and or arsenite of heavy metals as indicated by the Reactions 4.4-4.7:



Oxo Anions of Arsenic as Adsorbates

For inherent reasons arsenate is a better adsorbate than arsenite. The acid dissociation constants for arsenious acid, H₃AsO₃, and arsenic acid, H₃AsO₄, are as follows:

- H₃AsO₃ ↔ H⁺ + H₂AsO₃⁻ pK_{al} = 9.23
- H₂AsO₃⁻ ↔ H⁺ + HAsO₃²⁻ pK_{a2} =12.13
- HAsO₃²⁻ ↔ H⁺ + AsO₃³⁻ pK_{a3} = 13.4
- H₃AsO₄ ↔ H⁺ + H₂AsO₄⁻ pK_{al} = 2.22
- H₂AsO₄⁻ ↔ H⁺ + HAsO₄²⁻ pK_{a2} =6.98
- HAsO₄²⁻ ↔ H⁺ + AsO₄³⁻ pK_{a3} = 11.53

Obviously, H₃AsO₄ is a stronger acid than H₃AsO₃, and consequently, anions of the former are more easily produced leading to a stronger electrostatic attachment to a protonated adsorption site.

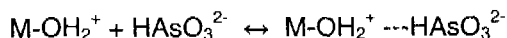
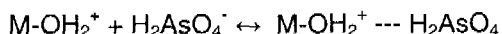
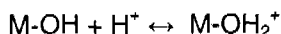
Tubewell waters may contain a whole variety of compounds ranging from simple inorganic to organic compounds. Under low pH, the organic species may react to give the Bronsted acids.

Mechanism of Adsorption on Cellulose⁵

The chief structural material of plants is the polymer cellulose. Wood consists of cellulose fibre together with a number of other non-cellulosic materials such as lignin, colouring matter, fats and waxes.

The OH groups of the sugar unit function as good adsorbing sites. Lignin, which binds the fibres together, and other non-cellulosic materials blocks these sites. Bleaching removes much of them from the surface and improves the adsorbing quality.

Some possible modes for adsorption of arsenate and arsenite onto a cellulose surface in acidic solutions are shown below:



The cellulose surface is represented by the M-OH group with which a hydrated proton forms an inner-sphere complex of the type M-OH₂⁺. The interaction between M-OH₂²⁺ and, say, HAsO₄²⁻ is of the outer sphere type. The interaction reduces the thickness of the electrical layers between particles bringing them down to precipitate onto the surface.

Sorption^d on Cellulose-Fe(OH)₃ Composite

Rust leaves a long-standing stain on cotton fabric. This encounter, although infrequent, motivated us to prepare a composite of newspaper pulp and Fe(OH)₃. Composites containing upto 3 per cent Fe(OH)₃, based on wet-weight of pulp, were found to be stable; above this concentration detachment of Fe(OH)₃ takes place.

d. Sorption is a general term for the processes of absorption, adsorption and chemisorption.

In a preliminary run a composite of 2.2g dry-weight, or 37 g wet-weight, of pulp and 1 g of $\text{Fe}(\text{OH})_3$ was found to sorb upto 120 mg of arsenic from synthetic solutions passed through columns with a flow rate of 1.8 mL per minute. Solutions that contained thousands of ppb in arsenic became safe after the treatment.

The column was regenerated by 0.1M NaOH elution⁶. The deep brown eluate does not produce red colour with KSCN but gives brown precipitate with dilute nitric acid.

Immobilizing the extractants on the cellulose surface facilitates solid-liquid separation which permits its use in conventional process equipment. Porous polymer beads with immobilized $\text{Fe}(\text{OH})_3$ was used previously in arsenic removal⁷.

The $\text{Fe}(\text{OH})_3$ impregnated porous support materials consisting of Al_2O_3 - TiO_2 were prepared and their interactions with arsenic in a water purification process were characterised⁸. A composite material that can trap arsenic may offer the best removal method.

4.4 DISCUSSION

Bijoypur clay from Mymensing and processed cellulosic materials like delignified jute, bleached saw dust and pulped newspaper were found to adsorb both As^{III} and As^{V} in solutions acidified with vinegar or hydrochloric acid.

Bijoypur clay and polystyrene adsorbed arsenic also in neutral medium.

Arsenic adsorption did not take place in a medium made basic by adding sodium hydroxide solution. Soils low in acidity and Fe^{III} cannot retain arsenic and allow it to move into solution.

Adsorption studies were carried out with adsorbents in batch and column type experiments using synthetic and source waters.

Cellulose- $\text{Fe}(\text{OH})_3$ composite in experimental filters sorbed the most arsenic. The composite shows potential for use in small-scale home treatment units. A workable exposure time, flow rate and extracting volume demonstrated arsenic removal at least to or even below the maximum contaminant level of 50 ppb. The sludge was regenerated by sodium hydroxide elution.

The observation is that almost everything adsorbs arsenic is in line with the ubiquity of the element.

Cations having high charge to size ratio such as trivalent iron and aluminium ions flocculate arsenic. Arsenic containing groundwater left out for 5 days precipitated arsenic because of air oxidation of iron and arsenite. The role, if any, of oxygen and carbon dioxide in precipitating arsenic by simple aeration can be tested by blowing the gases through freshly pumped-out groundwater.

4.5 RECOMMENDATIONS

Substances having layer lattices such as graphite and mica, rocks and minerals containing iron, clathrate compounds, molecular sieves and redox couple containing Zn- Fe system may adsorb the most arsenic.

Low-cost, small and fast treatment units for groundwater dearsenification can be developed using the types of materials cited.

The method of dearsenification of groundwater by simple aeration may be developed and used widely in small scale home treatment units.

Dug wells, because of their air exposure can give arsenic free water. Digging wells in arsenic prevalent areas can be tried.

The chemical speciation of any treated effluent must agree with the drinking water standards before it is recommended for drinking.

Arsenic recovery from the sludge should receive as much attention as the mitigation method itself.

4.6 REFERENCES

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5. SEASONAL VARIATION AND ARSENIC SPECIES

5.1 INTRODUCTION

For the quantification of arsenic in the field, the Natelson method, a colorimetric method, is currently being used. It can detect arsenic at 40 ppb. Arsine generated from arsenate or arsenite is reacted with silver diethyldithiocarbamate solution to produce a red solution that can be measured colorimetrically¹.

The hydride-generation method being applied commonly to the determination of arsenic species involves the digestion of a sample under UV radiation or in potassium persulfate followed by sodium borohydride reduction². The four arsines AsH_3 and $\text{Me}_x\text{AsH}_{3-x}$ ($x = 1-3$) are produced from their relevant precursors and are then determined following separation. The method ensures arsenic speciation in natural systems. Many arsenic compounds do not respond to simple digestion. They are treated under still more forcing conditions such as UV radiation combined with persulfate oxidation or microwave-assisted persulfate oxidation to generate arsines.

Total arsenic determination instead of separate speciation involves oxidation of a sample by digestion or ashing with mixtures of chemicals such as $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}_2$, $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-HClO}_4$ for wet ashing and $\text{MgO-Mg(NO}_3)_2$ for dry ashing³.

It may be mentioned that hydride-generation produces derivatives of arsenic and speciation requires some assumptions. To avoid uncertainty in speciation high-performance liquid chromatography and ion exchange methods are being used to separate species before determination. Often As^{III} is separated and determined in aqueous solutions by extraction with sodium diethyldithiocarbamate.

5.2 MASS SPECTROMETRY

Mass spectrometry is a recent addition in arsenic speciation methodology. It is a molecular recognition method normally followed by separation of the species by high performance liquid chromatography. The instrument is costly but the results obtained are impressive. In the most complete study to date only 10 species were separated and detected. These are shown in Table 6.

Table 6. The Organic Arsenicals Detected by Mass Spectrometry

| Sl. No. | Compound | Detection limit, ppm |
|---------|--------------------------------------|----------------------|
| 1 | Methylarsonic acid | 0.3 |
| 2 | p-Arsanilic acid | 0.1 |
| 3 | 4-Hydroxyphenylarsonic acid | 0.3 |
| 4 | Dimethylarsinic acid | 0.07 |
| 5 | 3-Nitro-4-hydroxy-phenylarsonic acid | 0.07 |
| 6 | 4-Nitrophenylarsonic acid | 0.1 |
| 7 | Arsenobetaine | 0.002 |
| 8 | Trimethylarsine oxide | 0.04 |
| 9 | Arsenocholine | 0.02 |
| 10 | Tetramethylarsonium ion | 0.02 |

5.3 ANALYTICAL METHODS FOR ARSENIC

As was mentioned arsenic is determined by a number of methods ranging from hydride generation using detection by colorimetry or spectrometry, and neutron activation to spectrophotometry using graphite-furnace atomic absorption or inductively coupled plasma-atomic emission spectrometry.

Electroanalysis, photometry, atomic absorption and activation analysis form the basis of standard tests for arsenic determination.

The silver diethyldithiocarbamate calorimetric method is valid for the concentration range of 5-250 ppb, atomic absorption-hydride generation for 1-20 ppb, atomic absorption-graphite furnace for 5-100 ppb⁴. Anodic stripping voltammetry is valid in the range of 2-200 ppb⁵.

More concentrated solutions can be analyzed after dilution. Activation methods involve neutron activation, PIXE and microwave induced plasma mass spectrometry.

5.4 STRIPPING VOLTAMMETRY

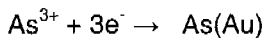
For small throughput analysis of As³⁺ and total-arsenic, As³⁺ + As⁵⁺, anodic stripping voltammetry, ASV, with a thin gold film deposited on glassy carbon

serves as the working electrode and a sensor for As^{3+} . This method is known to be the most cost-effective method and satisfies the sensitivity requirements.

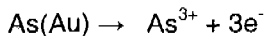
In the present work, ASV with a static gold film electrode was applied for As^{3+} and total-arsenic in groundwater.

The principle of ASV is based on the redox reaction of As^{3+} at the thin gold film on a glassy carbon electrode in HCl. The electrode reactions are as follows:

Reduction reaction:



Oxidation reaction:



In the reduction step, As^{3+} is reduced and deposited on the gold film electrode at 150 mV in 6M HCl as the supporting electrolyte.

The reverse scan, oxidation, is continued up to 500 mV with the scan rate of 50 mV s^{-1} in steps of 5 mV to completely strip off arsenic from the solid surface.

The maximum oxidation current is expressed as the function of concentration of arsenic.

In electrochemical analysis, like the present one, only As^{3+} responses. For the measurement of total-arsenic, $\text{As}^{3+} + \text{As}^{5+}$, As^{5+} in HCl is reduced to As^{3+} with Na_2SO_3 . After removing excess SO_2 with pure N_2 gas purging total-arsenic in the form of As^{3+} is measured.

5.5 EXPERIMENTAL WORKS

The samples were collected from Chatkhil, Noakhali once every month in a manner stated in Chapter 2 under General Experimental Section. They were then sent to SDC Environment Initiative, College more, Courtpara, Kushtia-7000 by Courier Service for analysis.

On occasion, The measurements were checked with Intronic Technology Centre, Dhaka, Bangladesh. The results were found to be in close agreement.

5.6 RESULTS

The average results of arsenic measurements, at different depths and their standard deviations are shown in Table 7.

Total-arsenic was determined in 79 and As^{III} in 24 groundwater samples collected from the nine locations over nine months during June 1998-February 1999. The results are shown in Table 8.

Graphically the results are presented in Figures 5-7. All concentrations are expressed in ppm. Figure 5 is a 3D bar-graph representing [As] Vs tubewell Locations.

Figure 6 is a 3D Bar graph representing [As] Vs depth in feet. The shaded bottom and the dark top of a bar stand respectively for the average and the standard deviations of [As].

Table 7: Arsenic Measurements at Locations 1-9: Mean Values and Standard Deviations

| Location No. | Depth, feet | Mean [As] , ppm | Standard deviation, ppm |
|--------------|-------------|-----------------|-------------------------|
| 1 | 90 | 0.374 | ±0.115 |
| 2 | 50 | 0.098 | ±0.073 |
| 3 | 40 | 0.137 | ±0.067 |
| 4 | 50 | 0.0869 | ±0.029 |
| 5 | 40 | 0.127 | ±0.055 |
| 6 | 35 | 1.001 | ±0.273 |
| 7 | 40 | 0.083 | ±0.333 |
| 8 | 75 | 0.534 | ±0.136 |
| 9 | 70 | 0.892 | ±0.284 |

Table 8: Speciation of Arsenic, in ppm, at Location Nos. 1-9

| Location No | Depth in Feet | Collection 5-6-98 Total As ^(III) | Collection 10-7-98 Total: As ^(III) % As ^(III) | Collection 7-8-98 Total As ^(III) | Collection 4-9-98 Total As ^(III) | Collection 12-10-98 Total As ^(III) | Collection 7-11-98 Total As ^(III) | Collection 9-12-98 Total As ^(III) | Collection 21-1-99 Total As ^(III) % As ^(III) | Collection 28-2-99 Total As ^(III) % As ^(III) |
|---|---------------|---|---|---|---|---|--|--|--|--|
| Mofiz Ullah, Halima Dighirpar, Chatkhil, Noakhali | 90 | 0.175 | 0.332 | 0.258 | 0.326 | 0.401 | 0.389 | 0.420 | 0.268 0.261 97 | 0.563 0.42475 |
| 2. Abkul Karim, Mozu Ali Bepari Bari, Afsarkhil, Chatkhil, Noakhali | 50 | 0.060 | 0.285 0.072 26 | 0.117 | 0.050 | 0.607 | 0.068 | 0.077 | 0.069 0.058 84 | 0.092 0.052 57 |
| 3. Yusuf Mia, Bepari Bari, Doulatpur, Chatkhil, Noakhali | 40 | 0.087 | 0.225 0.085 38 | 0.262 | 0.108 | 0.086 | 0.117 | 0.086 | 0.171 0.105 61 | 0.090 0.086 96 |
| 4. Atiq ulah, Alauddin Patwari Bari, Doulatpur, Chatkhil, Noakhali | 50 | 0.081 | 0.106 0.095 90 | 0.051 | 0.060 | Could not be collected | 0.145 | 0.070 | 0.102 0.083 81 | 0.080 0.061 76 |
| 5. Tofazzal Hossain, Mizan Pondit Bari, Chayani Tobga, Chatkhil, Noakhali | 40 | 0.111 | 0.246 0.075 30 | 0.066 | Gone under flood water | 0.101 | 0.163 | 0.121 | 0.102 0.080 78 | 0.107 0.045 42 |
| 6. Mustafizur Rahman, Mollah Bari, Chayani Tobga, Chatkhil, Noakhali | 35 | 0.844 | 1.058 | 1.332 | 1.174 | 0.968 | 1.056 | 1.048 | 1.155 0.823 71 | 0.370 0.296 80 |
| 7. Bishwambar Pal, Sridev Villa, Poura Ward No 2, Chatkhil, Noakhali | 40 | 0.065 | 0.211 0.064 30 | 0.143 | 0.048 | 0.047 | 0.061 | 0.047 | 0.060 0.048 80 | 0.064 0.050 78 |
| 8. Murad Hossain, Rowshan Ali Miaze Bari, Chatkhil, Noakhali | 75 | 0.722 | 0.569 0.075 13 | 0.640 | 0.491 | 0.397 | 0.367 | 0.423 | 0.721 0.513 71 | 0.474 0.440 93 |
| 9. Delwar Hossain, Abdur Rahman Bepari Bari, Chatkhil, Noakhali | 70 | 1.304 | 1.025 | 0.374 | 0.877 | 0.899 | 0.546 | 1.062 | 0.845 0.654 77 | 1.093 0.684 63 |

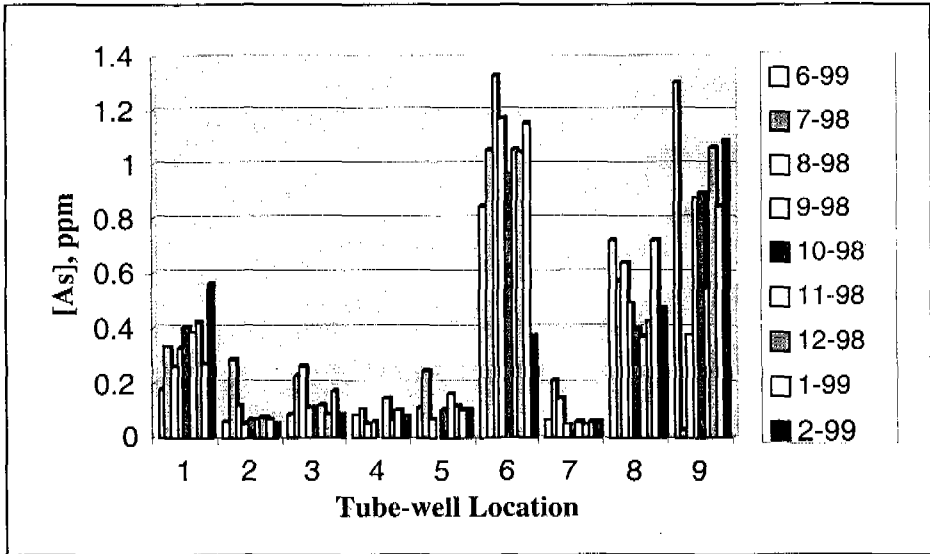


Figure 5 : [As] Vs Tubewells Location

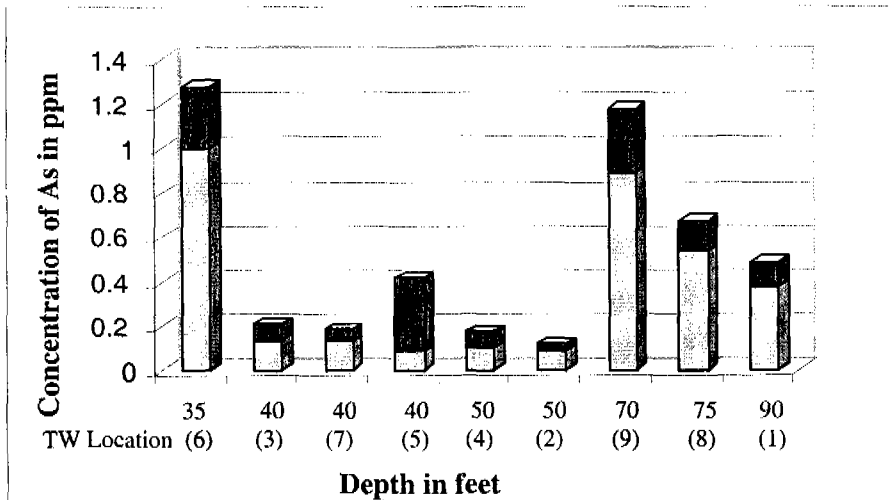
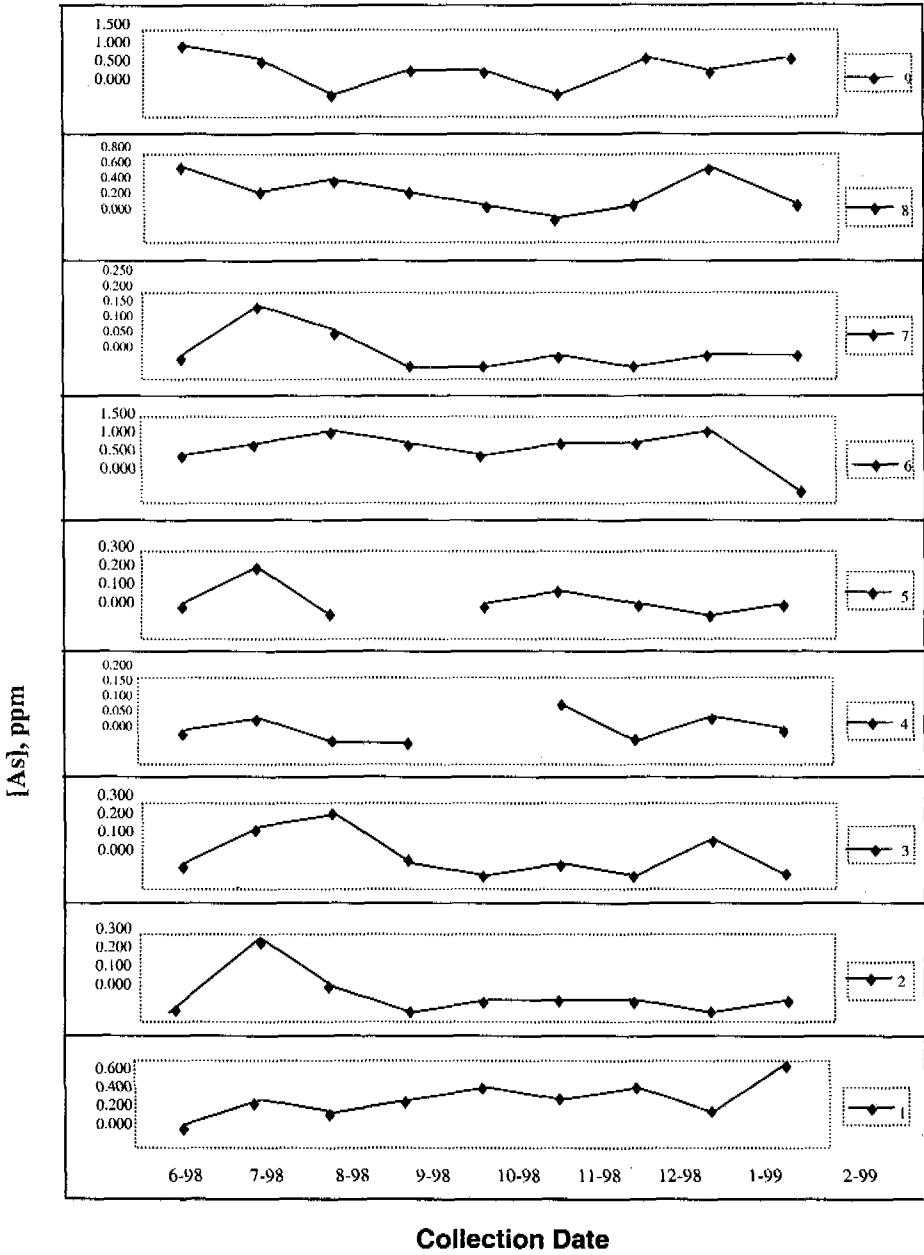


Figure 6 : [As] Vs Depth of Tubewells

The shaded and dark the part of the bar graph in Figure 6 represent the average results of 9 measurements and their standard deviations respectively.



Collection Date
Figure 7 : [As] Vs Sample collection Month

Figure 7 represents Month-wise Variation of [As] in all locations. During June-August the concentrations appeared relatively high.

Location Nos. 2-5 and 7 are in the range of 40-50 feet. Location Nos., 1,8 and 9 are in the range of 70-90 feet and are high in [As]. Location No. 6 is also high in [As] but only 35 feet deep.

The distribution of individual measurements at different depths at 9 locations is shown in Figures 8A-8C in the Appendix . Figures 8A, 8B and 8C are the Month-wise [As] Vs Depth plots. Arsenic concentrations within the 40-50 feet range touched the base line in all cases.

5.7 DISCUSSION

The amounts of total-arsenic found in these samples were in the range of 0.047-1.304 ppm with the proportion of As^{III} varying from 13-97 per cent.

The higher percentages of As^{III}, resulted from the simultaneous presence of higher percentages of Fe^{II} and or Mn^{II} in these samples. These ions enable the arsenite to resist oxidation during storage of the sample.

In these results it is seen that there is no systematic pattern in the distribution of total- arsenic with depth of different tubewells. However, it was noted that at a depth range of 40-50 feet the concentration of arsenic is relatively low; the concentration ranging from 0.087 to 0.137 ppm.

In the range of 70-90 feet as also at 35 feet arsenic level was found to be significantly high. These are considered as significant observations even if one takes experimental errors into consideration.

It is clear that, within the measurement period, small fluctuations in arsenic contents were observed, but in most cases, elevated concentrations were found during June–August which falls within rainy season. A previous study also recorded similar observations⁶.

After the great flood of 1998 the percentage of As^{III} appeared to have increased significantly. This is remarkable from the geochemical point of view.

At the end of the flood, the stagnant waters while trickling down, might have carried microbes down which reduces As^V to As^{III}.

5.8 RECOMMENDATIONS

A speciation study involving the same set of tubewells as well as few other nearby sets is needed in order to confirm the temporal variation of total-arsenic and arsenite and to confirm the distribution of arsenic in rainy and dry seasons.

The work can now be done with assured reliability particularly in view of the availability of efficient analytical centres.

The study needs to include more rural areas far away from each other in order to ascertain:

- A general pattern of seasonal variation.
- A relation between depth and arsenic concentration.
- A relation between arsenic concentration of groundwater and that of other species such as iron, manganese, aluminium, sodium, potassium, calcium, magnesium, chloride and phosphate.

A study in areas along rivers and canals could also establish the relationship between the arsenic concentration and the recharging of aquifers and the results could be compared with those obtained from a radio carbon dating technique.

Indeed, studies related to quantification of arsenic should be carried out extensively involving a large number of areas all over the country in order to work out a set of world class protection and preventive rules, that will be acceptable to environmental protection agencies, and will help to counter an arsenic calamity anywhere.

5.9 REFERENCES

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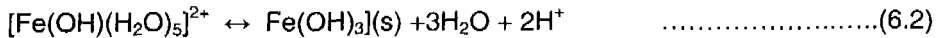
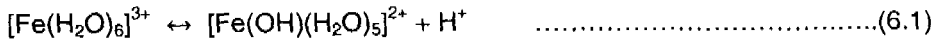
6. THE CO-OCCURRING IONS IN GROUNDWATER

6.1 INTRODUCTION

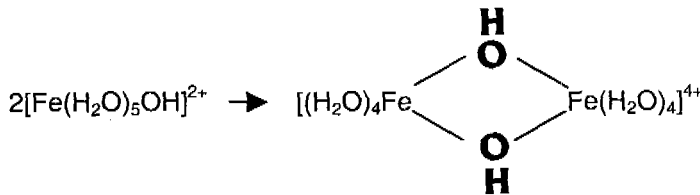
Chemical reactions taking place in natural waters are complex and the species thus produced are difficult to investigate.

As per rules of solubility, all sodium and potassium salts are water-soluble. The *d* and *p* block elements in natural waters do not exist as simple hydrated cations.

The Fe³⁺ cation, for example, in aqueous solution, reaches a state of maximum stability through the following hydrolyses:

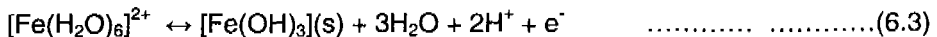


In some cases, polymerization to form colloidal hydroxyls occurs such as :

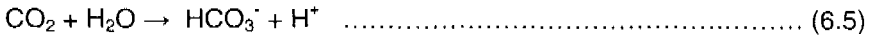


This hydroxyl polymer often precipitates as hydrated oxides, Fe₂O₃ · xH₂O. Similar reactions with the Al³⁺ ion are also possible. Relatively high levels of insoluble Fe^{III} and Mn^{IV} frequently appear in groundwater as colloidal materials, which are difficult to remove. These colloids are further stabilized by their hydrogen bonding with water or chelation of the metal centre with humic materials.

Iron and manganese in groundwaters are found in the soluble 2+ oxidation state because of the reducing conditions. In groundwater the level of iron^I seldom exceeds 10mg L⁻¹ and that of manganese is rarely higher than 2 mg L⁻¹. The basic method for removing Fe^{II} and Mn^{II} species is by oxidation to higher insoluble states. This oxidation is usually carried out by aeration. A high pH favours rapid oxidation as indicated by reaction 6.3.



The presence of Ca^{2+} ions in natural waters is facilitated by the bicarbonate, HCO_3^- anion, which can come from microbial degradation such as:



Clay mineral, contain large amounts of sodium, potassium, magnesium, calcium, iron and aluminum ions including traces of other metals in their structures. They also hold cations such as Ca^{2+} , Mg^{2+} , K^+ , Na^+ and NH_4^+ on ion exchange mechanism and protects them from leaching by water. Since many clays are readily suspended in water as colloidal particles, they may be leached and carried to lower soil levels .

The anions are sorbed by the positively charged colloidal particles at low pH. The nature of anion sorption depends on the type of anion. Chemical bonding sorbs phosphate and sulfate. Chloride and nitrate are sorbed by electrostatic attraction. A more specific binding mechanism may be involved in the sorption of fluoride, molybdate, selenate, selenite, arsenate and arsenite anions.

Arsenites of alkali metals are very soluble in water, those of alkaline earth metals are less so and those of the heavy metals are virtually insoluble². Oxoanions such as phosphate in natural waters are often found as polymeric species instead of simple monomers.

6.2 EXPERIMENTAL WORKS

For quantification, seven liters of water from Location No. 9, collected in June 1998, was evaporated to about 70 mL. The concentrate was then freeze dried; the solid residue so obtained weighed 1.576g. The concentration of the dissolved solid is 225 ppm.

6.3 RESULTS

The concentration of some co-occurring ions are shown in Table 9.

Table 9: Speciation of Co-occurring Ions in Groundwater from Location No. 9

| Loca- tion | Total Arsenic, ppm | Na^+ , ppm | K^+ , ppm | Fe^+ , ppm | Ca^{2+} & Mg^{2+} , ppm | Cl^- , ppm | PO_4^{3-} ,ppm |
|-----------------------|--------------------------|------------------------|-----------------------|--|---|------------------------|----------------------------|
| Locati on No. 9 | 1.304 | 20.55 | 5.052 | Present, But could not be estimated | 6.223 | 4.17 | 0.213 |

For comparison, some related drinking water standards are given in Table 10:

Table 10: Bangladesh and the US Standards for Drinking Water

| Parameters | Bangladesh Drinking Water Standards, ppm | US Drinking Water Standards, ppm |
|-----------------------------------|--|----------------------------------|
| Aluminium | 0.2 | - |
| Arsenic | 0.05 | 0.05 |
| Boron | 1.0 | - |
| Chromium | - | 0.05 |
| Cadmium | 0.005 | 0.01 |
| Copper | 1.00 | - |
| Cyanide, CN ⁻ | 0.1 | - |
| Fluoride | 1.0 | 1.4 -2.4 |
| Iron | 0.3-1.0 | 0.3 |
| Lead | 0.05 | 0.05 |
| Mercury | 0.001 | 0.002 |
| Nitrate | 10 | 10 |
| Radioactivity, Bq L ⁻¹ | 0.01 | 5 pCiL ⁻¹ |
| Selenium | 0.01 | 0.01 |
| Sodium | 200 | - |
| Total Dissolved Solid | 1000 | 500 |
| Temperature | 20-30°C | - |
| pH | 6.5-8.5 | 6.5-8.5 |

6.4 DISCUSSION

The concentration of sodium and potassium ions in groundwater from Location No. 9 is too low compared to their natural abundance of 23,000 and 21,000 ppm respectively in the earth's crust.

The ratio of the observed total dissolved solid to that of Bangladesh standard is 0.23 : 1, the ratio of prescribed sodium to that of Bangladesh standard on total dissolved solid is 0.2 : 1 and the ratio of observed sodium to that of Bangladesh standard on total dissolved solid is 0.02 : 1. From these values at least it is clear that the sodium content of the sample under investigation is very low, although its observed arsenic content is very high.

This indicates that most of the sodium in the soil around Location No.9 is held either by stable sodium containing minerals or this particular soil is not acidic.

An acidic soil holds protons and releases sodium ions by ion exchange. So, a low sodium in the groundwater sample is indicative of the basic nature of the soil.

The mitigation study clearly reveals that clay and cellulosic materials under acidic condition adsorb more arsenic than usual. So, Location No. 9 being a high arsenic site must have a basic soil. That is, basic soil is more prone to release arsenic but acidic soil is not.

It is likely that, because of acid rain seeping into groundwater, big cities like Dhaka would contain less arsenic and more sodium. If the acidity is due mainly to carbon dioxide, the groundwater of Dhaka would contain more calcium.

It must be born in mind that oxidation of microbes can be another source of underground carbon dioxide.

A previous hypothesis suggests that Dhaka has oxidised soil and a high percentage of Fe^{III} , which binds arsenic strongly and reduces its mobility³.

Groundwater from Location No. 9 is poor in calcium which is also in agreement with the explanation given. It is, therefore, most certain that the arsenic concentration in groundwater is inversely proportional to those of sodium, potassium and calcium as indicated by the relation:

$$[\text{As}] \propto \frac{1}{[M]} \quad (M = \text{Na}^+, \text{K}^+, \text{Ca}^{2+})$$

This relation is contrary to the notion that in groundwater high sodium content normally goes along with high arsenic concentration.

6.5 RECOMMENDATIONS

A comprehensive study is needed to establish the proposed interdependence between the concentrations of arsenic and those of sodium, potassium, calcium and also magnesium. The relationship will function as an index to predict indirectly the level of arsenic in a groundwater sample.

Similar relationships between arsenic and iron, aluminium, chloride, sulfate and phosphate in groundwater can be studied simultaneously.

This speciation study needs to be carried out in small and medium townships in order to see the effect of acid rain on the arsenic concentration of their groundwater.

The total dissolved solid, pH, and conductivity of the samples may also provide a guide in establishing relationships among various factors including those causing solubilisation of arsenic.

Apparently the presence of iron is a factor in lessening arsenic in groundwater. The use of scrap iron and iron ores in arsenic removal from groundwater supports this hypothesis.

6.6 REFERENCES

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APPENDIX

The month-wise variations of arsenic with depth of tubewell are presented in Figures 8A, 8B and 8C

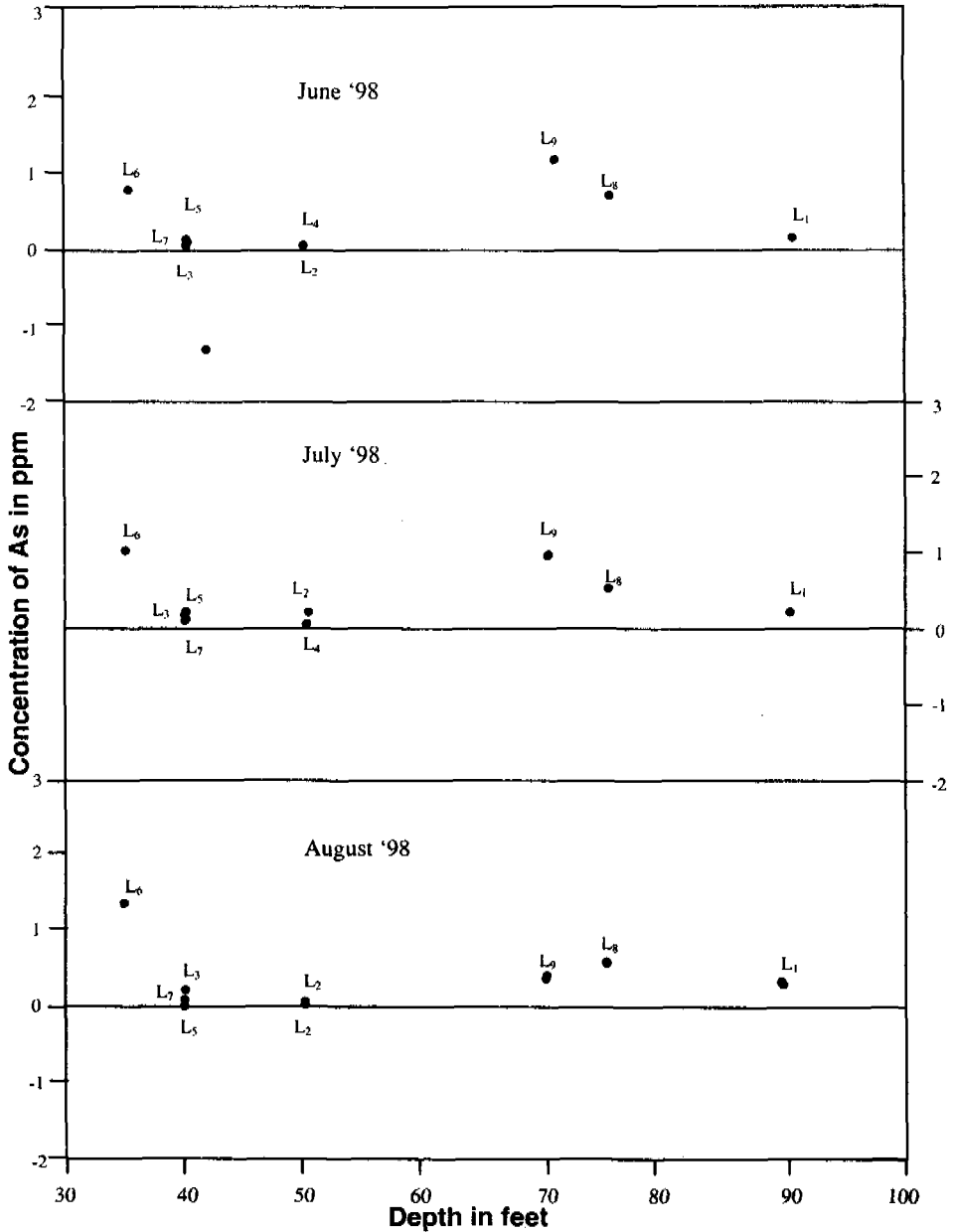


Figure 8A: Month-wise [As] Vs Depth of Tubewells: Jun-Aug 1998

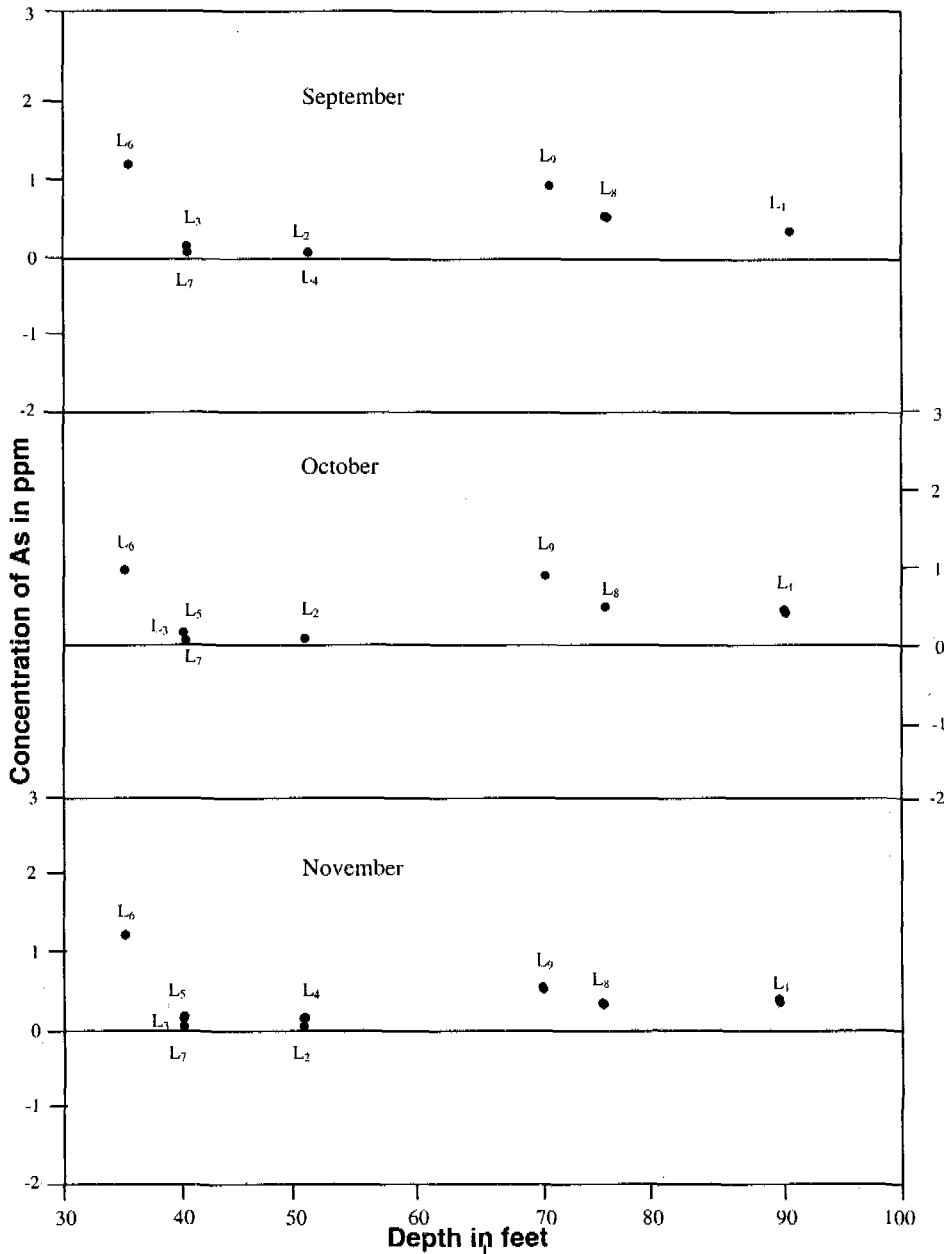


Figure 8B: Month-wise [As] Vs Depth of Tubewells: Sep-Nov 1998

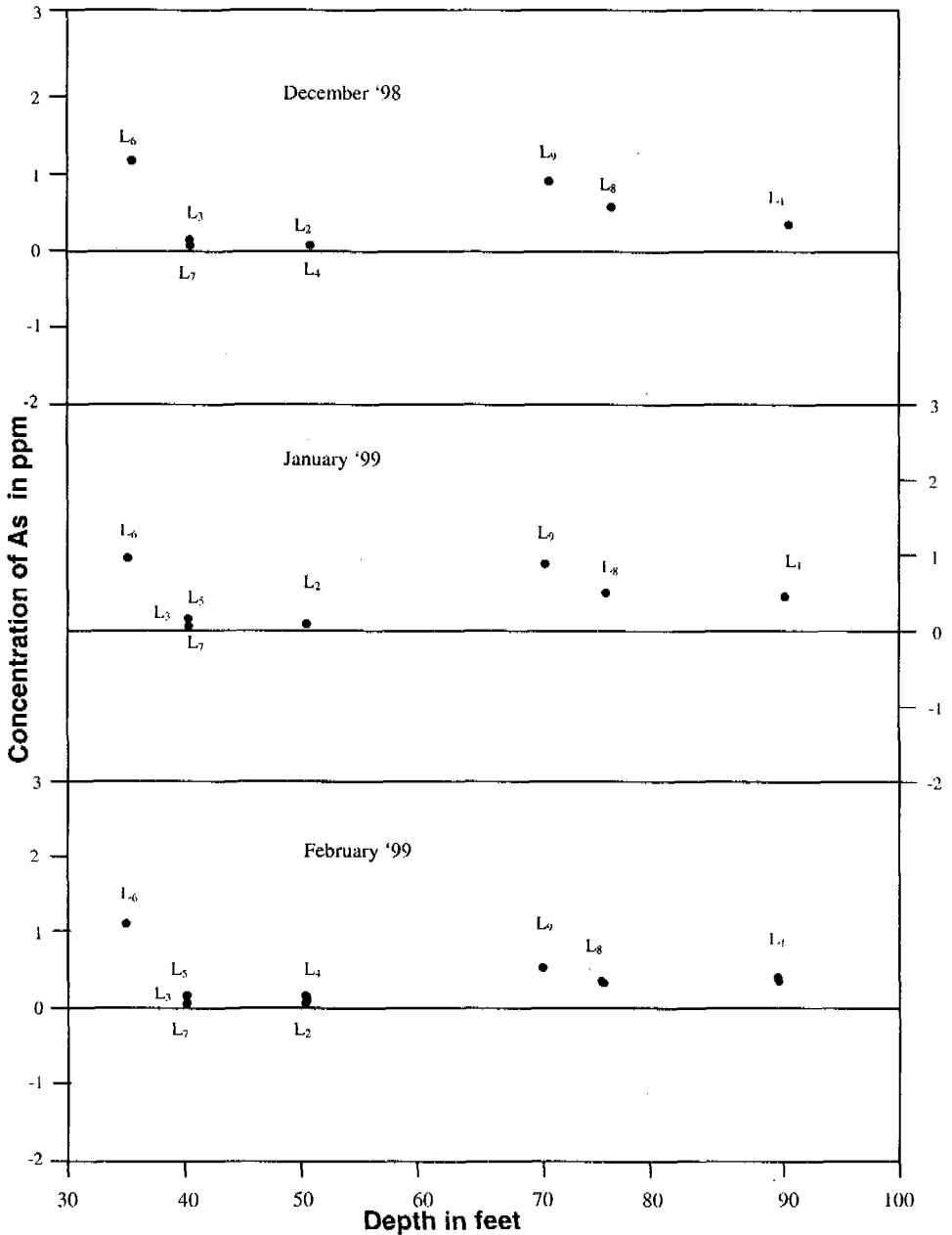


Figure 8C: Month-wise [As] Vs Depth of Tubewells:Dec1999-Feb1999

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